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ORGANOMETALLIC PHOTOCHEMISTRY AT THE SOLID/GAS INTERFACE. PHOTO--ETC(U)
MAY 81 J B KINNEY, R H STALEY, C L REICHEL N00014-75-C-0880

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High surface area SiO_2 ($400 \text{ m}^2/\text{g}$) functionalized first with SiH by reaction with $(\text{EtO})_3\text{SiH}$ and then reacted with $\text{Co}_2(\text{CO})_8$ yields $(\text{S})\text{SiCo}(\text{CO})_4$ ($\text{S} = \text{SiO}_2$). Photochemistry of $(\text{S})\text{SiCo}(\text{CO})_4$ exposed to various gases has been studied by using Fourier transform infrared photoacoustic spectroscopy, FTIR/PAS. Near-uv irradiation under ^{13}CO yields $(\text{S})\text{SiCo}(\text{CO})_n(^{13}\text{CO})_{4-n}$ and the reaction can be reversed by irradiation under CO . Irradiation under O_2 yields loss of metal carbonyl signals and CO and CO_2 are observed as gas phase products. Experiments with $^{18}\text{O}_2$ and with ^{13}CO -enriched $(\text{S})\text{SiCo}(\text{CO})_4$ show that CO_2 originates from CO initially bound to Co and O_2 in the gas phase. Ligand substitution by gas phase PF_3 , ethylene, propylene, isobutylene, or propyne can be detected when $(\text{S})\text{SiCo}(\text{CO})_4$ is irradiated in the presence of the gas. All photochemistry is consistent with loss of CO as the primary chemical result of photoexcitation of $(\text{S})\text{SiCo}(\text{CO})_4$. The FTIR/PAS technique is useful on sample sizes of $\sim 1 \text{ mg}$ and gives infrared spectra of comparable quality to transmission infrared of $\text{KBr}/(\text{S})\text{SiCo}(\text{CO})_4$ pellets. The FTIR/PAS technique requires no pretreatment or manipulation of the sample and the monitoring of surface and gas phase products can be done in situ.

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ORGANOMETALLIC PHOTOCHEMISTRY AT THE SOLID/GAS INTERFACE. PHOTOCHEMISTRY
OF SURFACE-CONFINED COBALT TETRACARBONYL MONITORED BY FOURIER TRANSFORM
INFRARED PHOTOACOUSTIC SPECTROSCOPY.

by

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Organometallic Photochemistry at the Solid/Gas Interface. Photochemistry
of Surface-Confined Cobalt Tetracarbonyl Monitored by Fourier Transform
Infrared Photoacoustic Spectroscopy

Abstract: High surface area SiO_2 ($400 \text{ m}^2/\text{g}$) functionalized first with SiH by reaction with $(\text{EtO})_3\text{SiH}$ and then reacted with $\text{Co}_2(\text{CO})_8$ yields $(\text{S})\text{SiCo}(\text{CO})_4$ ($\text{S} = \text{SiO}_2$). Photochemistry of $(\text{S})\text{SiCo}(\text{CO})_4$ exposed to various gases has been studied by using Fourier transform infrared photoacoustic spectroscopy, FTIR/PAS. Near-uv irradiation under ^{13}CO yields $(\text{S})\text{SiCo}(\text{CO})_n(^{13}\text{CO})_{4-n}$ and the reaction can be reversed by irradiation under CO . Irradiation under O_2 yields loss of metal carbonyl signals and CO and CO_2 are observed as gas phase products. Experiments with $^{18}\text{O}_2$ and with ^{13}CO -enriched $(\text{S})\text{SiCo}(\text{CO})_4$ show that CO_2 originates from CO initially bound to Co and O_2 in the gas phase. Ligand substitution by gas phase PF_3 , ethylene, propylene, isobutylene, or propyne can be detected when $(\text{S})\text{SiCo}(\text{CO})_4$ is irradiated in the presence of the gas. All photochemistry is consistent with loss of CO as the primary chemical result of photoexcitation of $(\text{S})\text{SiCo}(\text{CO})_4$. The FTIR/PAS technique is useful on sample sizes of $\sim 1 \text{ mg}$ and gives infrared spectra of comparable quality to transmission infrared of $\text{KBr}/(\text{S})\text{SiCo}(\text{CO})_4$ pellets. The FTIR/PAS technique requires no pretreatment or manipulation of the sample and the monitoring of surface and gas phase products can be done in situ.

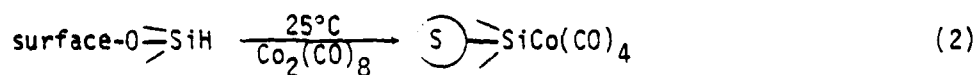
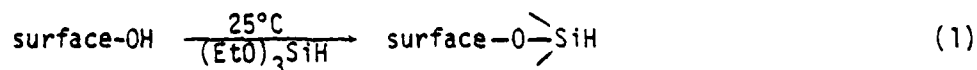
Organometallic Photochemistry at the Solid/Gas Interface. Photochemistry
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→ We wish to report the photochemistry of surface-confined -Co(CO)_4^- fragments exposed to reactive gases. Such photochemistry is of importance in establishing primary events following excitation of the molecular entity attached to the surface and is of relevance to the photoactivation of surface-confined catalysts.^{1,2} We apply, for the first time, the technique of Fourier transform infrared photoacoustic spectroscopy (FTIR/PAS)³ to monitor the photoreactions of a species on the surface including in situ monitoring of reactions involving a gas phase species. Without any sample manipulation or preparation, this technique has allowed characterization of the photochemistry of surface species with the molecular level specificity generally possible when infrared absorption spectroscopy is used to monitor reactions of metal carbonyls in homogeneous solution. The results herein establish FTIR/PAS as a technique of unequalled capability in monitoring such surface chemistry.⁴

The system studied is $(\text{S})\text{-SiCo(CO)}_4$ where (S) represents a high surface area silica ($\sim 400 \text{ m}^2/\text{g}$ from Alfa). The synthetic procedure follows from known reaction chemistry and was carried out according to the representation in (1) and (2).⁵ The functionalization of metal oxides such

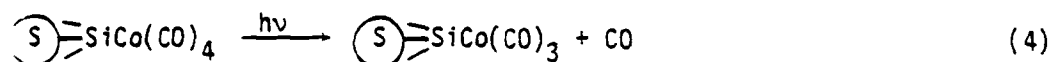


as SiO_2 using $(\text{RO})_3\text{SiR}'$ reagents⁶ and reaction of $\text{Co}_2(\text{CO})_8$ with R_3SiH to give $\text{R}_3\text{SiCo}(\text{CO})_4$ are both well-known.⁷ The reaction to prepare $(\text{S})\text{SiH}$ is established by transmission infrared of $\text{KBr}/(\text{S})\text{SiH}$ (10/1 by weight) pellets showing a feature at $\sim 2250 \text{ cm}^{-1}$ associated with the Si-H stretch; no feature in this region is observed for the SiO_2 prior to treatment with $(\text{EtO})_3\text{SiH}$. Absorption is also observed in the C-H region reflecting the fact that some residual EtO— groups remain. Reaction of $(\text{S})\text{SiH}$ with $\text{Co}_2(\text{CO})_8$ results in additional infrared absorptions in the metal carbonyl region at ~ 2110 (rel. o.d. = 0.3); 2050 (rel. o.d. = 0.5); and ~ 2020 (rel. o.d. = 1.0) cm^{-1} . The number of bands and their relative intensities accord well with bands expected for $(\text{S})\text{SiCo}(\text{CO})_4$ based on species such as $(\text{EtO})_3\text{SiCo}(\text{CO})_4$.^{1,7} From a combination of infrared and elemental analyses the coverage of $\text{SiCo}(\text{CO})_4$ is sub-monolayer ($\sim 10^{-11} \text{ mol/cm}^2$), and there is generally considerable SiH remaining after reaction with $\text{Co}_2(\text{CO})_8$.

Figure 1 includes a typical FTIR/PAS characterization of $\sim 1 \text{ mg}$ of $(\text{S})\text{SiH}/\text{SiCo}(\text{CO})_4$. The relative FTIR/PAS signals are proportional to infrared absorbances found for $(\text{S})\text{SiCo}(\text{CO})_4$ in KBr . For both forms of infrared the metal carbonyl signals are broader and less well-resolved than the spectral features for species such as $\text{R}_3\text{SiCo}(\text{CO})_4$ in alkane solution.^{1,7} The FTIR/PAS of the $(\text{S})\text{SiH}/\text{SiCo}(\text{CO})_4$ is just as good in terms of signal-to-noise as the FTIR/absorption and does not require palleting or other pretreatment of the sample. Quantities of sample required for FTIR/PAS are as small, or smaller, as typically used to prepare 1 cm diameter $\text{KBr}/(\text{S})\text{SiH}/\text{SiCo}(\text{CO})_4$ pellets.

The unique capabilities of the FTIR/PAS are revealed in the photochemical studies. Typically, a $\sim 1 \text{ mg}$ sample of $(\text{S})\text{SiH}/\text{SiCo}(\text{CO})_4$ is placed in the FTIR/PAS cell and irradiated at 25°C with the $300\text{--}400 \text{ nm}$ output from a 150 W Xe lamp focused to $\sim 1 \text{ cm}^2$; the input optical power to the sample

is $\sim 100 \text{ mW/cm}^2$. The undisturbed sample can then be characterized by FTIR/PAS.⁸ The first significant experiment concerns the results from irradiation of $(\text{S})\equiv\text{SiH}/\equiv\text{SiCo(CO)}_4$ when the cell contains 1 atm of ^{13}CO (90% ^{13}C). Figure 1 includes the FTIR/PAS spectrum that results after an irradiation of 15 min under ^{13}CO , pumping out all gases, and then introducing Ar for acoustic coupling. The spectra before and after irradiation under ^{13}CO establish the photochemistry represented by (3), a result that would be expected if (4) represents the primary chemical event following photo-

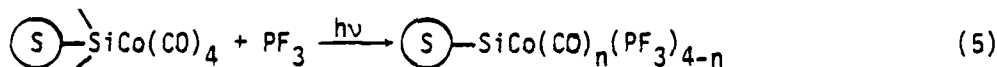


excitation. When irradiation is carried out for short periods of time, spectral changes are consistent with the sequential replacement of bound CO by ^{13}CO . The FTIR/PAS monitoring can be carried out without pumping out the cell, using the reactive gas as the acoustic coupler. When the gases are not pumped out the ^{13}CO is detected and ^{12}CO is detected as a gas phase photoproduct, as expected. Additionally, small amounts of CO_2 and $^{13}\text{CO}_2$ are detected as photoproducts (cf. below). Irradiation of $(\text{S})\equiv\text{Si(CO)}_n(^{13}\text{CO})_{4-n}$ for $n = 0$ under 1 atm CO results in the regeneration of $(\text{S})\equiv\text{SiCo(CO)}_4$ with $\sim 80\%$ recovery of the FTIR/PAS signal for the carbonyl species.

Chemically, these results establish CO loss as the principal result of photoexcitation of the $(\text{S})\equiv\text{SiCo(CO)}_4$. This finding parallels the conclusion drawn from studies of $\text{R}_3\text{SiCo(CO)}_4$ in homogeneous solution and $(\text{S})\equiv\text{SiCo(CO)}_4$ suspended in solution.¹ In particular, the FTIR/PAS shows little or no importance for photoinduced cleavage of the Si-Co bond that would lead to Co(CO)_4 or to the dimer $\text{Co}_2(\text{CO})_8$. With the FTIR/PAS technique, the data are much more easily obtained and without sample manipulation, compared to conventional infrared methods.

Additional photochemical results are consistent with the dissociative loss of CO from the surface. First, irradiation of the $(S)-SiCo(CO)_4$ under vacuum leads to disappearance of all metal carbonyl species. This disappearance is dramatically suppressed under CO, as expected. Under 1 atm Ar, irradiation leads to some decomposition, but the rate eventually declines, presumably due to the accumulation of CO in the cell. When decomposition is detected, CO and CO₂ are observed as gas phase photoproducts. Irradiation of the $(S)-SiCo(CO)_4$ under 1 atm O₂ leads to more rapid decline of the metal carbonyl signals, and a larger signal for gas phase CO₂ is observed, compared to reaction under Ar, Figure 2. Thus, O₂ is a reactive gas and presumably interacts with the photogenerated, coordinatively unsaturated $-SiCo(CO)_n$ species to lead to the oxidation of CO to CO₂. We estimate the CO/CO₂ product ratio to be ~3/1 when the irradiation is carried out under 1 atm O₂. Irradiation of $(S)-SiCo(CO)_4$ under ¹⁸O₂ leads to the formation of C¹⁸O¹⁶O and irradiation of ¹³CO-enriched $(S)-Si(CO)_4$ under ¹⁸O₂ leads to ¹³C¹⁸O¹⁶O. These results establish the source of CO₂ to be CO originally bound to Co and O₂ in the gas phase. The Co product is likely some form of Co-oxide; PAS in the visible region is consistent with this conclusion.⁹

FTIR/PAS can also be used to monitor photosubstitution of the $(S)-SiCo(CO)_4$ using gas phase entering groups such as PF₃ and olefins, Figure 3. At 25°C, the chemistry represented by (5) is detectable. The main



infrared feature is at ~2000 cm⁻¹ and is associated with $(S)-SiCo(CO)_3PF_3$ with the PF₃ occupying an axial position trans to the $-Si-$, as found for R₃SiCo-(CO)₃P(OPh)₃ prepared by photosubstitution.^{1,10} Irradiation of $(S)-SiCo(CO)_n(PF_3)_{4-n}$ under 1 atm CO leads to the regeneration of a large fraction of the $(S)-SiCo(CO)_4$. Irradiation of $(S)-SiCo(CO)_4$ under ethylene or propylene at 25°C yields loss of all metal carbonyls; Et₃SiCo(CO)₃(alkene) was shown previously to decompose at 25°C.¹ But irradiation of the

$\text{(S)}-\text{SiCo(CO)}_4$ at -50°C under ethylene, propylene, isobutylene, or propyne and monitored by FTIR/PAS at that temperature, leads to the generation of new surface metal carbonyl species, Figure 3. The signal at $\sim 1990\text{ cm}^{-1}$ would logically be attributed to $\text{(S)}-\text{SiCo(CO)}_3(\text{alkene})$, where the alkene is trans to the $-\text{Si}-$, paralleling solution studies. A signal that grows in at $\sim 2050\text{ cm}^{-1}$ for ethylene, propylene, or propyne, but not isobutylene, is unidentified at this time. Such a signal could be due to another isomer of the $\text{(S)}-\text{SiCo(CO)}_3(\text{alkene})$ where the alkene is cis to the $-\text{Si}-$, or the peak could be due to multiple substitution. This point is currently under investigation, but it does appear that the species associated with the $\sim 2050\text{ cm}^{-1}$ peak is a primary product, since it appears even at short irradiation times. Interestingly, the $\sim 2050\text{ cm}^{-1}$ peak does not appear in low temperature irradiations of $\text{Ph}_3\text{SiCo(CO)}_4$ in solutions containing 1-pentene or ethylene, but the $\text{Ph}_3\text{Si}-$ group may offer more steric restriction than the $\text{(S)}-\text{Si}-$.

To summarize, we have established the primary photoreaction of $\text{(S)}-\text{SiCo(CO)}_4$ to be loss of CO. This can be exploited to study the oxidation of CO by O_2 , to prepare inert or labile substitution products, and to elaborate the mechanism of the reactions of immobilized, photogenerated, coordinatively unsaturated intermediates. The technique of FTIR/PAS is shown to be a molecular specific tool having unique capabilities for the study of photo-reactions of the surface species on high surface area supports.

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- There are a number of techniques useful for obtaining vibrational spectra of surface species, cf. "Vibrational Spectroscopies for Adsorbed Species", A. T. Bell, M.L. Hair, Eds., ACS Symposium Series, **1980**, 137, American Chemical Society, Washington, D.C. The FTIR/PAS would appear to offer advantages when monitoring both surface and gas phase reaction products in situ.
- In a typical procedure, ~1 g of high surface area SiO_2 having some -OH available is suspended in ~25 ml of alkane solvent containing excess $(\text{EtO})_3\text{SiH}$ at 25°C under N_2 . The solution is stirred for 24 h and then filtered to collect a solid. After repeated washing the solid exhibits an infrared signal at $\sim 2250\text{ cm}^{-1}$ associated with Si-H. Infrared transmission experiments indicate that there is ~6.1 mol per cent >SiH .^{1b} The powder is then reacted with excess $\text{Co}_2(\text{CO})_8$ in alkane solution under N_2 at 25°C for 24 h. After repeated washing, the solid still exhibits an infrared peak at $\sim 2250\text{ cm}^{-1}$ (~3.4 mol per cent SiH) and signals at 2110, 2050, and $\sim 2020\text{ cm}^{-1}$ characteristic of $\text{>SiCo}(\text{CO})_4$ (~1.9 mol percent).^{1b} Reaction of the powder with $\text{Co}_2(\text{CO})_8$ also leads to some decomposition of the $\text{Co}_2(\text{CO})_8$ to leave a Co-oxide/hydroxide on the surface.^{1b} Samples were exposed to vacuum for 20 min at 25°C prior to any experimentation to remove any O_2 or H_2O from the surface.
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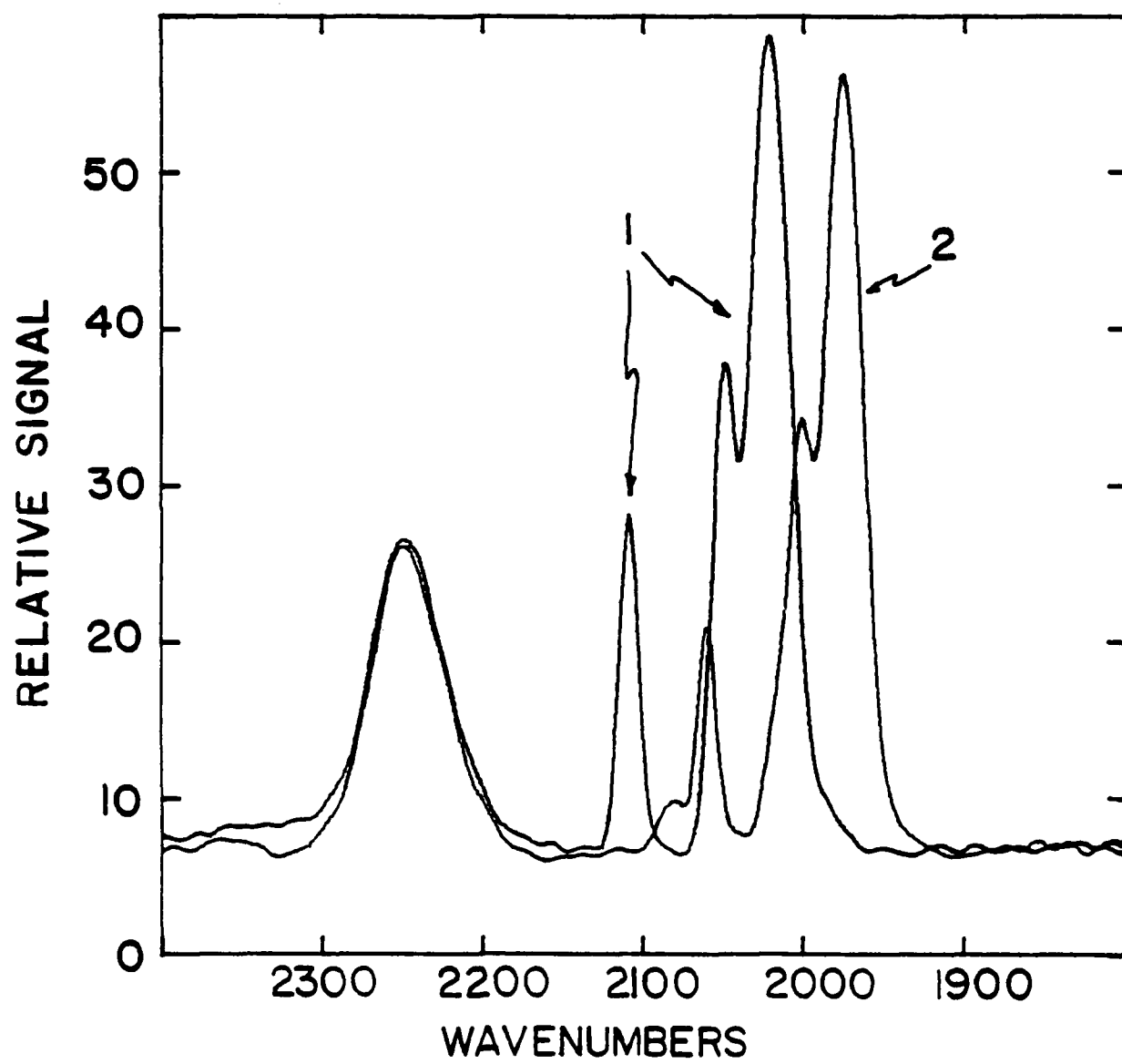
8. FTIR/PAS spectra were obtained using a Nicolet 7199 FTIR with a gas microphone photo-acoustic detector of our own design that allows control of the sample environment. The details are to be published independently by JBK and RHS. Data collection for 8 cm⁻¹ resolution spectra typically take 4 min. The acoustic coupling gas in all cases was 1 atm Ar (<1 ppm H₂O, O₂) except when monitoring gas phase products as in photolyses under O₂.
9. The Co-oxide product is detected as an absorber in the visible at ~620 nm.^{1b} Monitoring a sample by FTIR/PAS and by PAS in the visible shows the decline of metal carbonyl to be accompanied by the growth of the ~620 nm feature attributed to Co-oxide.
10. Many metal carbonyls undergo photosubstitution under PF₃, Geoffroy, G.L.; Wrighton, M.S. "Organometallic Photochemistry", Academic Press: New York, 1979, including Co carbonyls related to those under study here: Udovich, C.A.; Clark, R.J. Inorg. Chem., 1969, 8, 938.

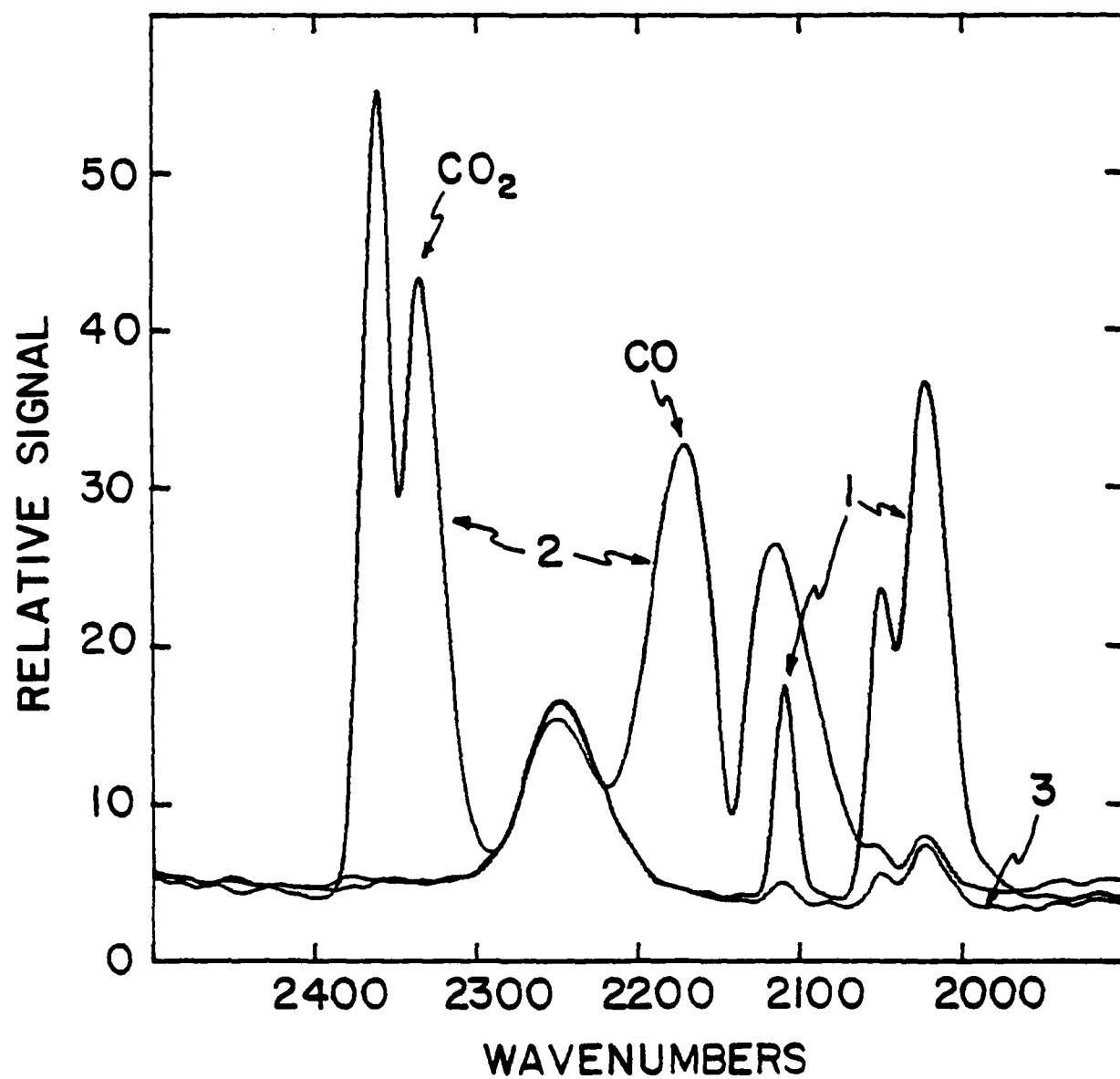
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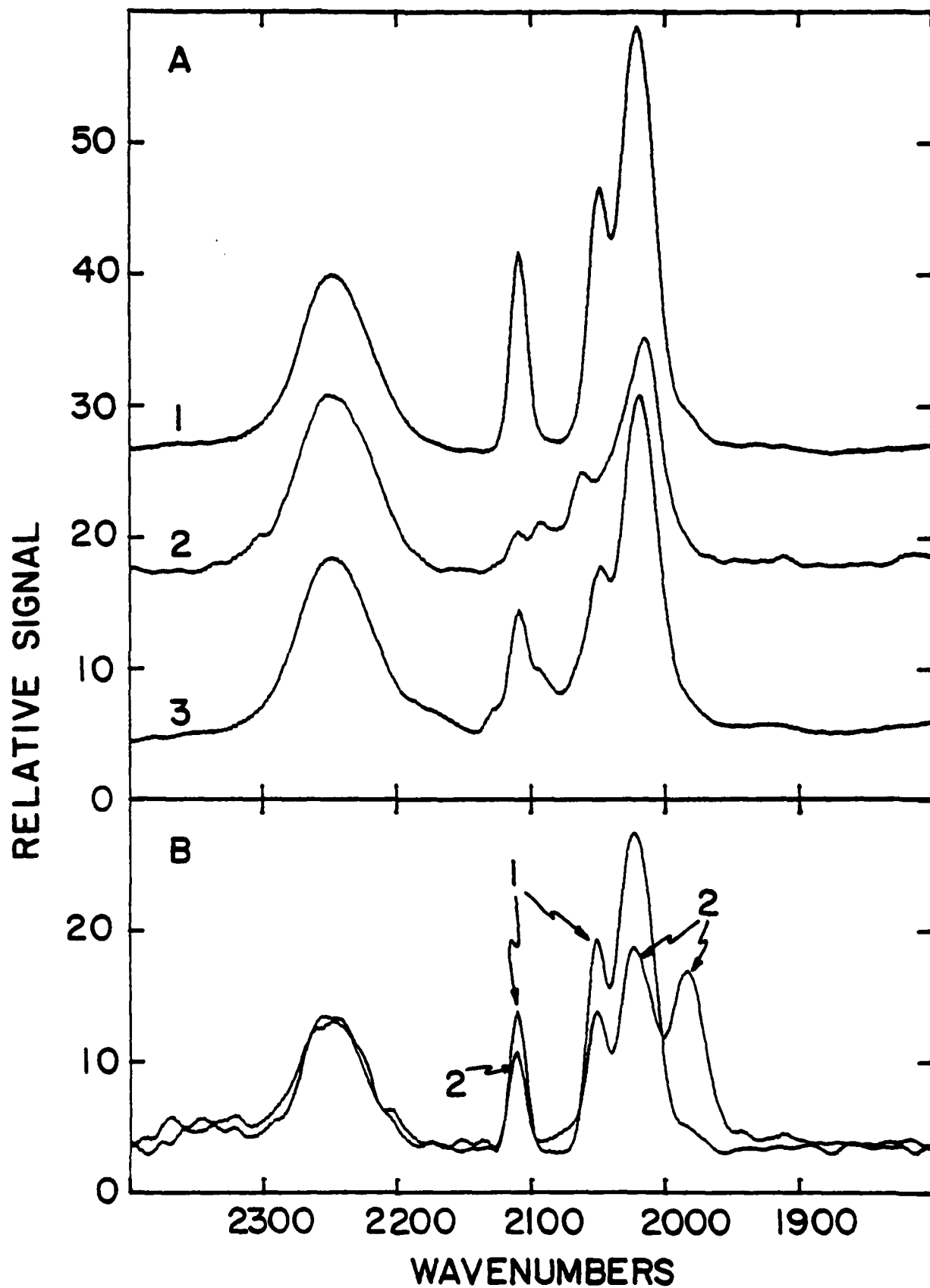
Figure 1. FTIR/PAS spectrum before, curve 1, and after, curve 2, 20 min near-uv irradiation of $(S)-SiCo(CO)_4$ under 1 atm ^{13}CO . In each case the acoustic coupling gas is 1 atm Ar. The spectral changes are consistent with the photochemical generation of $(S)-SiCo(^{13}CO)_4$. No ^{13}CO exchange occurs in the dark at 25°C on the timescale of this experimentation.

Figure 2. FTIR/PAS spectrum before, curve 1, and after, curve 2, 20 min near-uv irradiation of $(S)-SiCo(CO)_4$ under 1 atm O_2 . For spectra 1 and 2 the acoustic coupling gas is the 1 atm O_2 . Spectrum 2 shows gaseous CO and CO_2 photoproducts. Spectrum 3 is after evacuating the sample chamber to remove all gases and introducing O_2 at 1 atm as the acoustic coupling gas.

Figure 3. (A) Curve 1 is the initial FTIR/PAS spectrum of a sample of $(S)-SiCo(CO)_4$ and curve 2 is the spectrum obtained after near-uv irradiation, of the sample characterized in 1, for 10 min under 1 atm PF_3 . The product is $(S)-SiCo(CO)_n(PF_3)_{4-n}$. Curve 3 is the spectrum that results when the sample characterized in 2 is irradiated under 1 atm of CO to regenerate $(S)-SiCo(CO)_4$. These spectra are recorded using 1 atm Ar as the coupling gas. (B) Spectral changes accompanying the near-uv irradiation of $(S)-SiCo(CO)_4$, curve 1, at low temperature, $-50^\circ C$, under ~ 100 torr isobutylene for 10 min to form $(S)-SiCo(CO)_3(isobutylene)$, curve 2.







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